THE CHEMICAL COMPOSITION OF THE ESSENTIAL OIL OF THE LARCH

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The chemical composition of the oleoresins, turpentines, and essential oils of coniferous varieties have been considered in a number of publications [1-6]; the least investigated are the essential oils of coniferous varieties. Great attention is being devoted to the study of the monoterpene hydrocarbons, which are the main components of the oil, and only a few publications contain information on the composition of the sesquiterpene hydrocarbons [7-9]. We have found no information in the literature on the high-boiling fraction of the essential oil of various species of larch.

We have previously reported the presence in the essential oil of the larch of 40 components, of which 14 compounds were identified [10] and have published information on the composition of the monoterpene hydrocarbons of the essential oil of a number of species of larch growing in the USSR [10].

In the present paper we give the results of investigations of the chemical composition of the essential oil of the four main species of larch growing in the USSR (*Larix sibirica* Ldb., *L. dahurica* Turcz., *L. decidua* Mill., and *L. sukaczewii* Djil), and also the Altai variety of the Siberian larch (*L. sibirica* Ldb. *Oec. altaica* Scat.), performed under linear temperature-programming conditions.

Figures 1-3 give chromatograms of the analysis of samples of different species of larch. The linear programming of the temperature considerably shortens the time of a complete analysis (to 45 min) [10]. The selection of the optimum conditions for analysis (selective sorbent, high sensitivity, and other methodical expedients) enabled fairly sharp chromatograms of the oxygen-containing and sesquiterpene components to be obtained.

We have detected and confirmed the presence of 16 chemical compounds previously known in the essential oil of the larch, 10 of which we have been able to identify by the method of adding pure samples, and six from literature information in accordance with the retention characteristics.

In a preparative gas—liquid chromatography, from the essential oil of the larch we isolated fractions corresponding to the boiling points of the components — citral (geranial and neral), camphor, bornyl acetate, caryophyllene, longifolene, terpineol, σ- and γ-cadinenes, and azulene — and measured their retention characteristics.

For their reliable identification, the same substances were isolated by preparative gas—liquid chromatography from plants in which they were present in appreciable amounts and were added to the samples essential oils of larch being studied.

Citral, consisting of a mixture of two isomers — geranial and neral — was isolated on a preparative chromatograph from the oil of *Pelargonium capitatum* Ait. The addition of citral to the essential oil of the larch gave an increase in the size of peaks 23 and 24 (peak 23 from 1.52 to 55.42%; peak 24 from 13.71 to 29.26%), which enabled these peaks to be identified as citral.

Camphor was identified by the addition of pure camphor (an increase in peak 30 from 0.53 to 6.80%).

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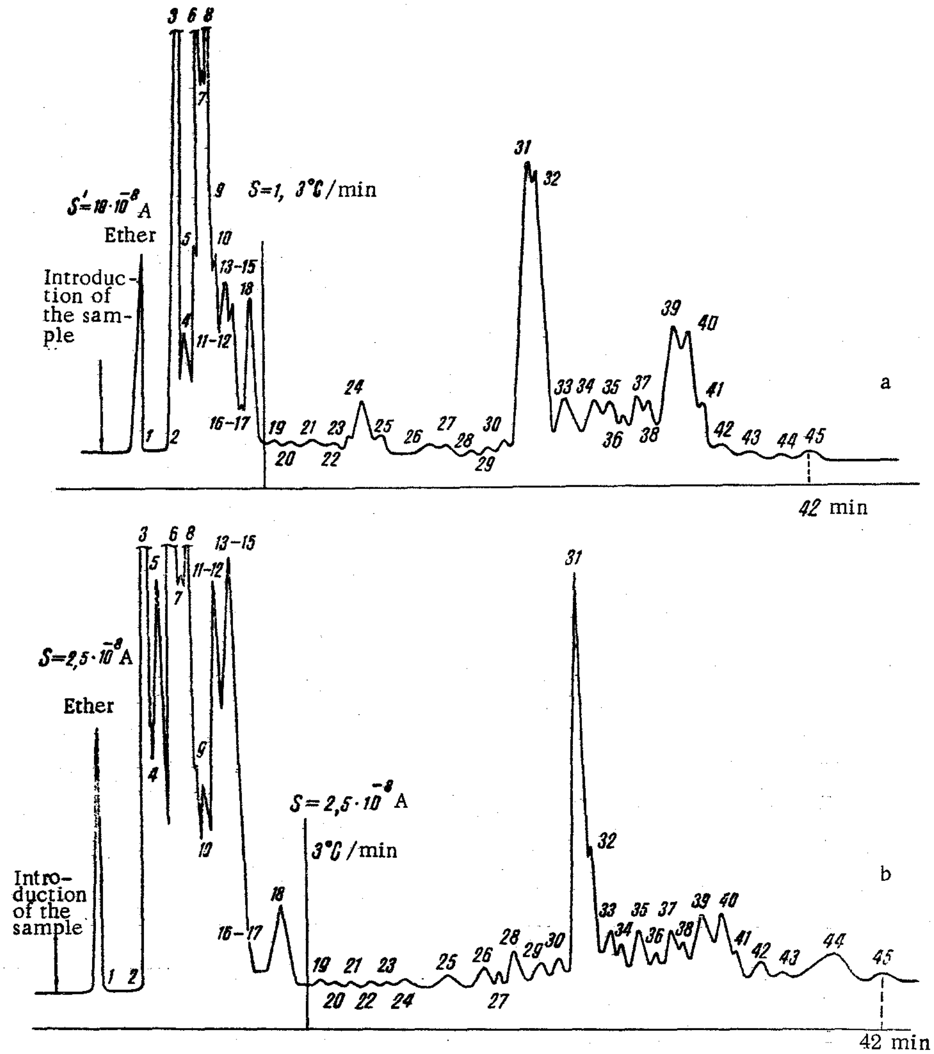

Fig. 1. Separation of the essential oil of the Siberian larch (a) and its Altai variety (b) (for the symbols of the components, see Table 1).

Bornyl acetate was isolated on a preparative chromatograph from the oil *Abies sibirica* Ldb. On its addition to the essential oil of the larch, peak 31 increased from 1.23 to 3.82%.

Longifolene was isolated from the oil of *Pinus longifolia* Roxb. When it was added to the larch oil, peak 33 increased from 1.38 to 2.8%.

Terpineol was synthesized in the laboratory. When it was added to the oil, peak 37 increased from 2.5 to 4.75%.

A mixture of σ-cadinene and γ-cadinene was isolated from the oil of *Juniperus communis* L. When it was added to the larch oil, peak 39 increased from 1.89 to 2.37% and peak 40 from 0.58 to 1.5%.

Chamazulene was isolated from the oil of *Matricaria chamomilla* L. When it was added to the larch oil, the area of peak 41 increased from 2.7 to 5.85%.

Humulene (α-caryophyllene), α-murolene, β-bisabolene, α-curcumene, elemazulene, and calamene were identified from their retention characteristics according to literature information [12, 13].

The results of the investigation of the composition of the essential oil showed that the qualitative composition of the oxygen-containing and sesquiterpene compounds in all the species of larch studied is the same (Table 1).

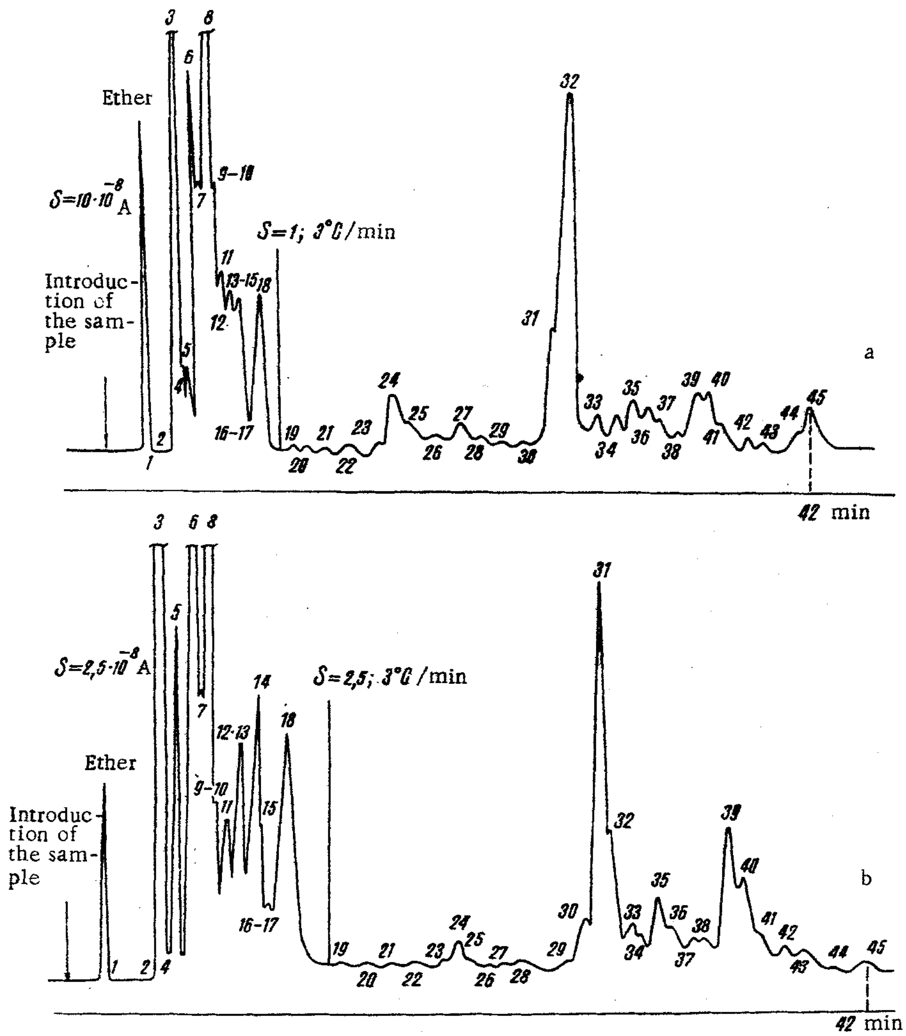

Fig. 2. Separation of the essential oil of Sukachev's larch (a) and of the Dahurian larch (b) (for the symbols of the components, see Table 1).

The main components of the essential oil are monoterpene compounds, among which α-pinene, β-pinene, and Δ^3-carene predominate. Thus, the proportion of monoterpenes in Sukachev's larch is 90.7%, in the Siberian larch 92%, in the Altai variety of the Siberian larch 85.5%, in the essential oil of the Dahurian larch 80.4%, and in the European larch 79.8%. Among the oxygen-containing compounds, bornyl acetate predominates, and of the sesquiterpenes the main components are the caryophyllenes and cadinenes.

Among the total components, the unidentified compounds were present in traces or very small amounts (tenths and one hundredths of a per cent). However, in our opinion, attention must be devoted to their identification in connection with questions of the biogenesis of the terpenes in plants, etc. This is the object of our further investigations. In Table 2, the components mentioned are shown together with the sesquiterpenes, and the calculation of the percentages in the essential oil mixture has been performed without taking the monoterpenes into account. The region of the sesquiterpene hydrocarbons is shown as if separately (see Figs. 1-3), and the consideration of the mutual influence of these compounds is apparently not unimportant both for the purposes of biogenesis and for the purposes of systematics.

The highest amount (21.2% on the total amount of components) of oxygen-containing and sesquiterpene components is observed in the essential oil of the European larch. Here, bornyl acetate, caryophyllene, and the cadinenes predominate. The essential oil of the Dahurian larch also contains a fairly considerable amount (about 20%) of these components, among which bornyl acetate and the cadinenes predominate. Bornyl acetate and caryophyllene

TABLE 1. Chemical Composition of the Essential Oils of Larches (%)

No.	Component	log V_R (PEGA)	Species of larch				
			Siberian (Altai variety)	European	Dahurian	Siberian	Sukachev's
1	Santene	2,065	Tr.*	Tr.	Tr.	Tr.	Tr.
2	Tricyclene	2,181	Tr.	Tr.	Tr.	Tr.	Tr.
3	α-Pinene	2,212	13,4	17,2	16,2	18,0	12,9
4	Fenchene	2,272	Tr.	Tr.	1,4	Tr.	Tr.
5	Camphene	2,310	5,2	5,3	2,4	1,8	3,8
6	β-Pinene	2,378	30,0	5,5	18,6	12,0	7,1
7	Myrcene	2,389	3,0	1,0	4,5	0,4	0,7
8	Δ^3-Carene	2,420	2,6	20,8	16,5	34,0	34,0
9 10	α-Phellandrene + α-terpinene	2,438	Tr.	3,0	3,3	4,6	7,2
11	Dipentene	2,465	6,1	5,2	2,0	1,8	1,9
12	β-Phellandrene	2,490	3,0	2,8	0,7	4,0	3,8
13	Cineole	2,522	3,2	3,4	3,2	7,2	5,7
14 15	γ-Terpinene + p-cymene	2,544	16,6	9,8	8,7	3,2	7,7
16	X_1	2,579	1,2	Tr.	0,5	Tr.	Tr.
17	X_2	2,611	Tr.	Tr.	0,7	Tr.	Tr.
18	Terpinolene	2.642	1,1	5,9	1,7	5,0	5,9
19	X_3	2,753	Tr.	Tr.	Tr.	Tr.	Tr.
20	X_4	2,788	Tr.	Tr.	Tr.	Tr.	Tr.
21	X_5	2,815	Tr.	Tr.	Tr.	Tr.	Tr.
22	X_6	2,831	Tr.	0,2	Tr.	Tr.	Tr.
	Citral -						
23	geranial	2,880	Tr.	Tr.	Tr.	0,1	0,1
24	neral	2,899	0,2	1,0	0,1	0,3	0,4
25	X_7	2,903	0,2	0,2	0,1	0,1	0,2
26	X_8	2,924	0,1	0,2	0,2	0,1	0,2
27	X_9	2,939	0,5	Tr.	0,2	0,1	0,1
28	X_{10}	2,953	Tr.	0,7	0,2	0,1	Tr.
29	X_{11}	2,980	0,2	Tr.	0,2	0,1	0,1
30	Camphor	2,991	0,4	0,5	0,2	0,2	0,1
31	Bornyl acetate	3,008	5,2	1,8	3,5	0,8	1,1
32	Caryophyllene	3,017	1,5	3,1	1,0	1,5	3,8
33	Longifolene	3,029	0,7	0,7	1,0	0,5	0,3
34	X_{12}	3,041	0,5	1,3	0,8	0,3	0,2
35	X_{13}	3,053	0.6	2,5	1,2	0,3	0,6
36	Humulene (α-caryophyllene)	3,061	0,2	0,7	1,6	0,2	0,3
37	Terpineol	3,072	0,6	1,3	0,7	0,5	0,2
38	α-Murolene	3,083	0,3	0,5	1,0	0,5	0,3
39	σ-Cadinene	3,093	1,2	1.9	2,6	0,8	0,4
40	γ-Cadinene	3,107	0,9	2,7	2,0	0,9	0,5
41	Chamazulene	3,117	Tr.	0,5	1,4	0,2	0,1
42	β-Bisabolene	3,130	0,1	0,2	0,7	0,2	0,1
43	α-Curcumene	3,140	Tr.	0,1	0,4	0,1	Tr.
44	Elemazulene	3,149	1,1	Tr.	0,5	0,1	Tr.
45	Calamene	3,173	0,1	Tr.	Tr.	Tr.	0.2

*Tr. — amount less than 0.1%.

predominate in the essential oil of Sukachev's larch. The smallest amount of oxygen-containing and sesquiterpene compounds is present in the essential oil of the Siberian larch (about 8%), but among them the cadinenes, caryophyllene, and bornyl acetate again predominate. Bornyl acetate and caryophyllene also predominate in the essential oil of samples from the Altai variety of the Siberian larch.

The oils of the species of larch considered also contain chamazulene, its maximum amount being found in the Dahurian larch.

EXPERIMENTAL

The collection and preparation of the samples of raw material for the extraction of the essential oil were performed in experimental geographical cultures of larches created in the spring of 1955 in a series of fresh loamy soils in the training and experimental leskhoz [forestry farm] of the Voronezh Institute of Wood Technology.

For investigation we took 1-yr shoots from seven to 10 trees of the Siberian larch (Altai variety), the European larch, the Dahurian larch, and Sukachev's larch. The samples were taken in the winter period, when the essential oil is present in a relatively stable state.

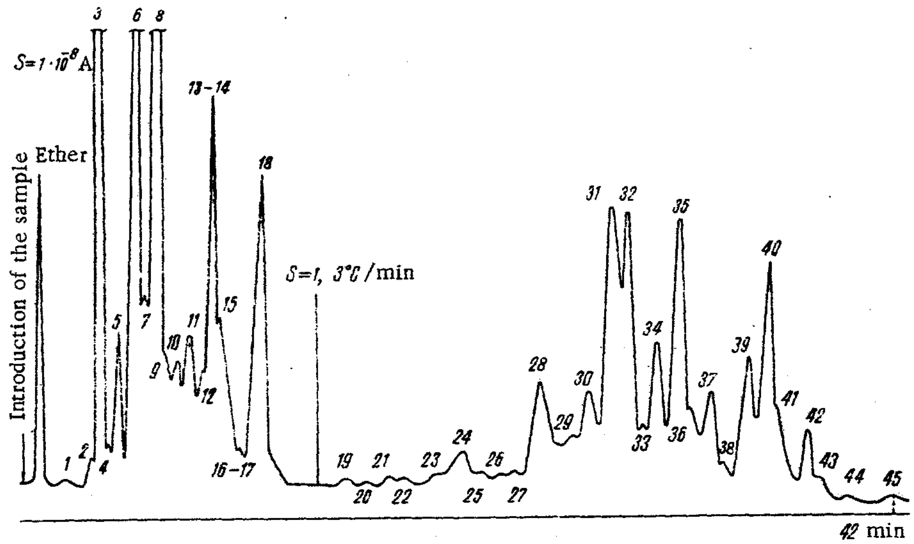

Fig. 3. Separation of the essential oil of the European larch (for the symbols of the components, see Table 1).

TABLE 2. Amounts of Oxygen-Containing and Sesquiterpene Compounds in the Essential Oils of Larches (%)

No.	Component	Species of larch				
		Siberian (Altai variety)	European	Dahurian	Siberian	Sukachev's
	Total monoterpenes (18 components)	85,5	79,8	80,4	92,0	90,7
1(19)	X_1	Tr.	Tr.	Tr.	0,1	0,3
2(20)	X_2	Tr.	0,2	Tr.	0,1	0,3
3(21)	X_3	Tr.	Tr.	Tr.	0,2	0,2
4(22)	X_4	0,3	0,9	0,2	0,4	0,4
	Citral					
5(23)	geranial	Tr.	0,2	0,1	0,5	0,8
6(24)	neral	1,3	5,0	0,7	3,6	4,3
7(25)	X_5	1,5	1,2	0,2	1,2	2,1
8(26)	X_6	0,7	1,0	0,4	1,7	1,8
9(27)	X_7	3,2	0,1	1,2	1,2	0,8
10(28)	X_8	Tr.	3,3	1,2	0,9	0,3
11(29)	X_9	1,5	0,2	1,2	1,3	0,9
12(30)	Camphor	2,9	2,3	1,5	2,6	1,2
13(31)	Bornyl acetate	35,9	9,6	18,4	9,2	13,4
14(32)	Caryophyllene	10,2	15,4	4,8	18,9	33,2
15(33)	Longifolene	4,5	3,3	5,0	6,5	3,9
16(34)	X_{10}	3,2	6,5	3,8	4,4	2,6
17(35)	X_{11}	4,2	12,1	6,1	3,2	6,7
18(36)	Humulene (α-	1,4	3,7	8,0	1,8	3,8
19(37)	caryophyllene)	3,8	6,6	3,2	6,9	3,0
20(38)	Terpineol	1,9	2,4	5,7	6,5	3,0
21(39)	α-Murolene	8,1	9,3	12,9	10,2	5,2
22(40)	σ-Cadinene	6,1	12,9	10,2	11,4	6,4
23(41)	γ-Cadinene	Tr.	2,6	7,1	2,8	1,6
24(42)	Chamazulene	0,8	0,9	3,5	2,3	0,8
25(43)	β-Bisabolene	0,2	0,3	1,8	1,5	0,5
26(44)	α-Curcumene	7,7	Tr.	2,8	0,4	0,4
27(45)	Elemazulene	0,6	Tr.	Tr.	0,2	2,1

*The numbers according to Table 1 are given in parentheses.

Samples of the needles and shoots of *Abies nordmanniana* (Stev.) Spach. were taken in the plantations of the Yalta mountain-forest reserve (age of the trees 100-120 years), of *Pinus longifolia* Roxb. in the collection of the Institute of Mountain Horticulture and Floriculture, Sochi (age of the trees 90-100 years), and samples of the needles of *Juniperu communis* L. in the Professor Kozo-Polyanskii Botanical Garden of Voronezh State University.

Distillation and Analysis of the Essential Oil. The essential oil was distilled off from the 1-yr shoots ground to 0.1–0.5 cm in a Klevendzher apparatus at 96°C for 4 h [14].

The essential oils were analyzed on a Tsvet-3 chromatograph with a 6 m × 3 mm column. The stationary phase was poly(ethylene adipate), 12 wt.% on diatomite with a grain size of 0.25-0.5 mm. The temperature of the column was programmed from 120 to 200°C, the rate of rise of temperature was 3°C/min, the temperature of the evaporator was 150°C, the sample volume was 3 μl, the carrier gas was helium at a rate of flow of 35 ml/min, flame ionization detector, sensitivity 10^{-8} A. The rate of flow of air was 300, and of hydrogen 30, ml/min.

The individual compounds were isolated from the essential oils on a type PGK-3 preparative gas—liquid chromatograph (column 10 m × 20 mm). The stationary phase was poly(ethylene adipate), 20 wt.%, on diatomite with a grain size of 0.5-1 mm. The column temperature was 160°C, the carrier gas helium, and the volume of the sample subjected to separation 10 ml.

SUMMARY

The essential oils of various species of larch have been separated by gas—liquid chromatography under conditions of linear temperature programming.

Of the 45 compounds present in each of the essential oils, 32 components have been identified, 16 of which have not previously been found in larch essential oil.

The chemical compositions of the oxygen-containing and sesquiterpene hydrocarbons of four species and one variety of larch have been studied. It has been shown that there is no quantitative difference between the compositions of the individual species of larch and only their quantitative compositions differ.

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